



Poisoning of Pt/C catalysts by CO and its consequences over the kinetics of hydrogen chemisorption

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ABSTRACT

The initial rate of hydrogen dissociation was studied as a function of irreversible CO coverage at 353 K on 30 wt.% Pt/carbon catalysts (Pt/C) prepared according to different processes. The Pt/C catalysts exhibit similar Pt dispersion ($D \sim 0.07$) and mean Pt particles size ($d_p \sim 16$ nm). The turnover frequency (number of hydrogen molecules dissociated per CO-free surface Pt atom) was determined as a function of CO coverage from 0.0 to 0.8. The evolution of TOF as a function of CO coverage is in agreement with the model of CO adsorbing on low coordination sites (edges, corners) and then spreading across the faces to grow islands as Brandt suggested in the past (R.K. Brandt, M.R. Hughes, L.P. Bourget, K. Truszkowska, R.G. Greenler, Surf. Sci. 286 (1993) 15–25). At high CO coverage (~ 0.8), TOF depends on the process by which the Pt/C catalyst was prepared. In particular, a Pt/C elaborated according to a colloidal process exhibits a low sensitivity to CO poisoning with an increase of TOF by one order of magnitude.

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1. Introduction

Since several decades, polymer electrolyte membrane fuel cells (PEMFC) are an incentive domain of research for mobile applications, e.g. vehicles, phones, laptops ... PEMFC fuelled by dihydrogen are of particular concern. Among the sequence of elementary steps, hydrogen dissociation, occurring at anodes containing catalytic metal nanoparticles (Pt generally), is an important step in the overall process. The reaction is normally fast however CO at tenths ppm level is often present due to the process of hydrogen production. CO is chemisorbed strongly on the sites active for hydrogen dissociation, leading to a progressive inhibition hydrogen dissociation on the electrode. The adsorption of dihydrogen on group VIII transition metals has been extensively studied in the past [1–11], with some focus on the kinetics of dihydrogen adsorption on platinum [9,11] using solid state NMR, thermal desorption mass spectrometry, or other techniques. The adsorption and/or oxidation of carbon monoxide on platinum surfaces has also been studied in the past [12–15]. An interesting aspect of these studies is the possible influence of the size of platinum crystallites on hydrogen and carbon monoxide heats of adsorption [16–19].

However, these studies mainly concern the thermodynamics of hydrogen chemisorption. Actually, the catalytic process occurring at

the Pt anode involves first hydrogen dissociation and then spillover of H atoms onto the carbon support with transformation into H⁺ and e[−]. The effect of CO coverage on the hydrogen oxidation reaction (HOR) was recently evaluated in HClO₄ electrolyte solution through the kinetically controlled current density [6]. It was shown that the current per remaining hydrogen adsorption sites free from CO remains roughly constant up to $\theta_{CO} = 0.6$ for reaction temperature above 343 K. In this regard, whatever the extend of CO coverage on Pt, θ_{CO} , a point of importance is the kinetics of hydrogen dissociation on the remaining free Pt sites. To our knowledge, this aspect was never addressed so far, namely what is the rate of hydrogen dissociation as a function of θ_{CO} ? Does it decrease, increase or keep constant? The present work aims to answer these questions. For the first time we show here that the turnover frequency of hydrogen dissociation (h^{−1}, specific rate per free surface Pt atom) may increase upon increasing CO coverage and depends on the way by which the Pt/carbon catalyst was prepared. The experiments were carried out on homemade and commercial Pt/carbon (Pt/C), the catalytic component of the anode membrane.

2. Experimental

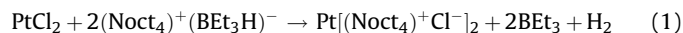
2.1. Materials

The preparation method of the Pt/C catalysts was based on the synthesis of colloidal precursors using the procedure described by

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Bönnemann et al. [20], modified as already described in the literature [21,22]. The main steps of the synthesis method employed are described hereafter. First, the reducing agent is synthesised by mixing a stoichiometric amount of tetra(octyl)ammonium bromide $(\text{Noct}_4)^+\text{Br}^-$ and potassium triethylhydroborate $\text{K}^+(\text{BEt}_3\text{H})^-$ in tetrahydrofuran (THF) as a solvent. After elimination of the precipitated KBr, a solution of tetra(octyl)ammonium triethylhydroborate $(\text{Noct}_4)^+(\text{BEt}_3\text{H})^-$ was obtained which reduced the platinum salt according to the following reaction:



In this way, the platinum nanoparticles are stabilized by $(\text{Noct}_4)^+\text{Cl}^-$, which acts as a surfactant protecting the metal particles with its long alkyl chain [23,24]. The colloid particles were then adsorbed on Vulcan XC72 carbon, previously treated for 4 h at 673 K in nitrogen to remove physisorbed molecules, in order to obtain a catalyst loading of 30 wt.% Pt as determined by thermogravimetric analyses. The final materials were recovered after surfactant removal, either by mild calcination at 573 K (Pt/C-coll-C), or by washing in ethanol (Pt/C-coll-W). The platinum content was further determined by elemental analysis (Service Central d'Analyse du CNRS, Vernaison). These were consistent with thermal analyses results. A commercial 30% Pt/Vulcan XC72 provided by E-TEK (Pt/C-E-TEK) was studied for the sake of comparison. Reduction of the catalysts was performed at 523 K overnight under static hydrogen (purity better than 99.99%).

2.2. Apparatus

Adsorption isotherms of carbon monoxide or hydrogen were determined by using a homemade adsorption set-up based on manometric measurements. The full description of this apparatus has already been published elsewhere [25]. The textural properties of the catalysts were determined by nitrogen sorption using a Micromeritics ASAP 2010 set up and according to the classical BET method.

TEM analysis was performed with a JEOL 1200 EX II instrument operating at 80–100 kV. The samples were prepared by suspending and sonicating the reduced catalysts in acetone and placing a drop of the suspension on a carbon copper grid. In order to obtain the average platinum particle size on the catalyst surface, $\text{dp}_s = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$, the distribution of platinum particles size was determined from examination of 1000–1500 particles on several representative micrographs for each catalyst.

2.3. Methods

Our experimental approach consists of two phases, the determination of the CO adsorption isotherms and the kinetics of hydrogen dissociation on the Pt surface under controlled CO coverages. The first step of our experimental procedure is the careful activation of the catalyst in hydrogen. This reduction was performed at 473 K, using static hydrogen (1 bar) for 8 h. The catalyst was then evacuated at 0.01 Pa at the same temperature and finally cooled down at 353 K. A first adsorption isotherm of CO was then obtained at 353 K, which corresponds to both irreversibly and weakly adsorbed CO. At full CO coverage, the catalyst was evacuated for 30 min at 0.01 Pa. A second adsorption isotherm was then obtained which corresponds to weakly adsorbed CO only. The knowledge of the two adsorption isotherms allows to carry out the chemisorption of hydrogen at 353 K on a platinum surface with controlled pre-coverage (vide supra) of irreversibly adsorbed CO. This represents the second step of the experimental procedure.

3. Results and discussion

As an example, Fig. 1 presents the adsorption isotherm of total and weakly adsorbed CO on Pt/C-coll-W. The dispersion of the Pt phase ($D = \text{Pt}_s/\text{Pt}_t$) was estimated from the CO uptake extrapolated at zero pressure and taking the CO/Pts stoichiometry of unity, with the usual assumption that each CO species is adsorbed on a single Pt surface site. As a reference for full CO coverage we have chosen the total CO uptake at zero pressure (vide supra).

From the difference between total and weakly adsorbed CO, the amount of irreversibly bonded CO can be determined at a given equilibrium pressure, and therefore the fraction $(1 - \theta_{\text{CO}})$ of CO-free Pt sites after evacuation of CO (θ_{CO} : fractional coverage of surface platinum sites with irreversibly bonded CO). It must be emphasized that the part of irreversibly bonded CO on the different materials can only be indirectly determined by deriving the difference between the two adsorption isotherms presented in Fig. 1. The knowledge of the irreversible-CO adsorption isotherm, obtained by this difference, allows us to choose a CO coverage for which the initial rate of hydrogen dissociation will be then determined. In practice, a known amount of CO is introduced in the sample cell which may be adsorbed both reversibly and irreversibly, especially when close to saturation of the catalysts surface. Knowing the two sorption isotherms allows determining the part irreversibly adsorbed onto the catalyst for this known amount of CO. The reversibly adsorbed CO is then evacuated for 30 min at 0.01 Pa.

We have then studied the kinetics of hydrogen dissociation at 353 K by feeding the sample cell with a single pulse of 60 Pa of hydrogen. We have taken great attention on several points: (i) from preliminary experiments we have checked by combining manometric and gravimetric experiments that hydrogen chemisorption does not result in desorption of irreversibly bonded CO; (ii) upon hydrogen admission, there is a very fast expansion of hydrogen gas in the measuring chamber, the corresponding pressure drop obviously being not related with hydrogen adsorption. This hydrogen flux was estimated by performing hydrogen expansion

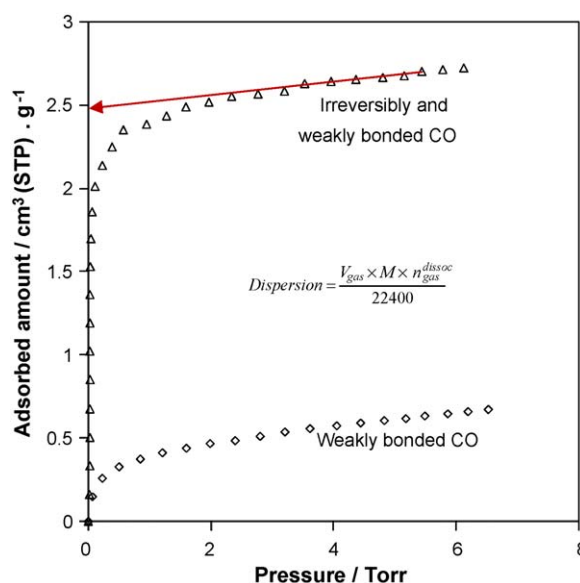


Fig. 1. Isotherms of CO chemisorption on Pt/C-coll-W at 353 K; (Δ) total bonded CO, weakly and irreversibly (\diamond) weakly bonded CO. The dispersion can be estimated from the extrapolation of the saturation plateau to the Y-axis. The inset shows the formula employed to derive the metal dispersion in which V_{gas} is the amount of gas chemisorbed, M is the molar mass of the metal and $n_{\text{gas}}^{\text{dissoc}}$ the stoichiometry coefficient of the chemisorption process.

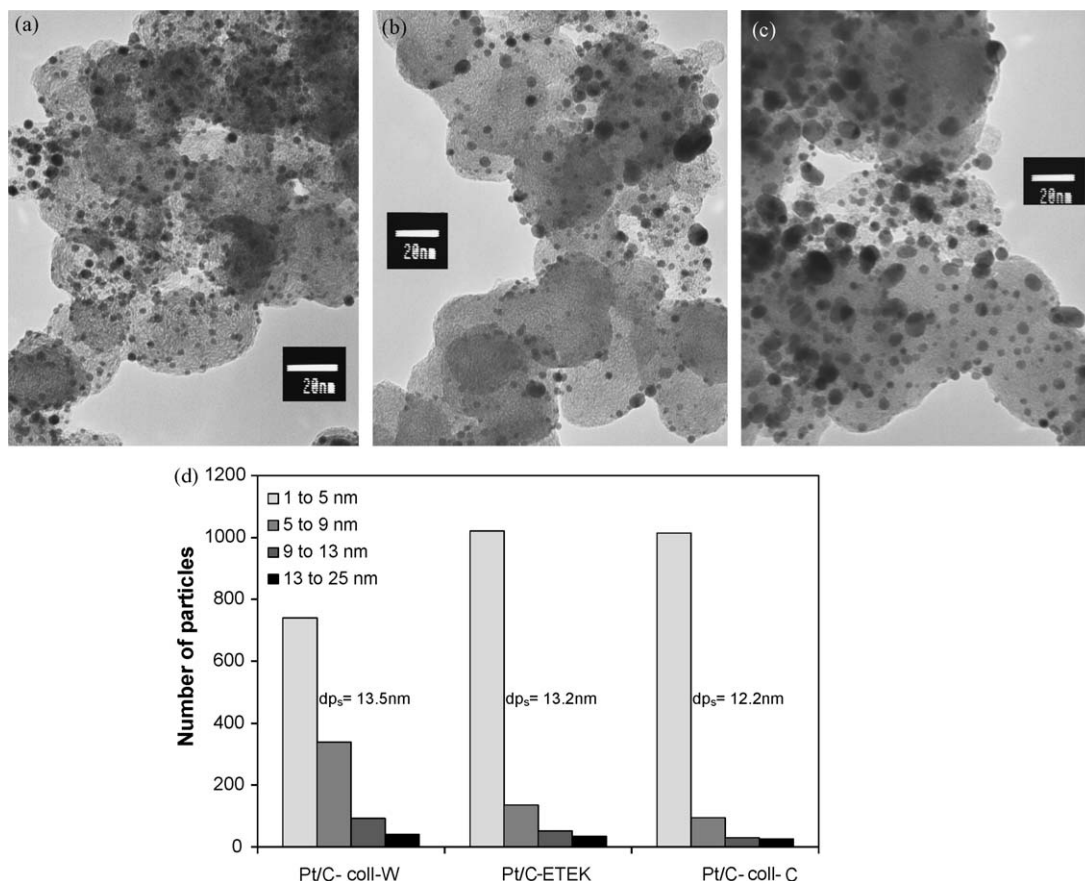


Fig. 2. Transmission electron micrographs of the three samples. (a) Pt/C-ETEK, (b) Pt/C-Coll-C, (c) Pt/C-Coll-W, (d) particle size distribution for the three catalysts.

in the empty adsorption cell or by helium expansion in the adsorption cell full of sample at 353 K. In both experiments, equilibrium pressure was reached immediately in less than 1 s in the adsorption cell. Therefore, to determine the initial rate of hydrogen adsorption, the very first pressure measurements were not taken into account (<1 s). Finally, both the very small amount of hydrogen introduced ($\sim 1 \mu\text{mol}$) and the fact that the initial hydrogen dissociation rate was determined in the range of 1–3 s, ensures that hydrogen covers about 50% of the free platinum surface sites in the most critical conditions of a θ_{CO} around 0.80. This small coverage of hydrogen ensures that the kinetics of hydrogen dissociation will be effectively measured rather than the much slower process of hydrogen spillover to the carbon support. The standard error made from this linearization was estimated. Because the slopes are in the same order of magnitude regardless of the sample, similar standard errors were found, always less than 8% of the determined slope for any of the initial rates of adsorption.

Table 1 presents some main characteristics of the catalysts. It is worth noting that the catalysts exhibit comparable Pt dispersion with D values from 0.063 to 0.070. It must be also emphasized that the Pt particle size usually ranges between 2 and 4 nm before thermal treatment. However, after activation it is well known that the particle size increases due to sintering (not presented here).

Table 1
Some textural characteristics of the catalysts.

Sample	Microporous volume ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	wt.% Pt	Pt dispersion (D)
Pt/C-coll-C	0.115	66	30	0.069
Pt/C-coll-W	0.199	152	30	0.063
Pt/C-ETEK	0.300	252	30	0.068

There is an approximate correlation between dispersion and mean particles size on the surface: dp_s (nm) $\sim 1.1/D$; it comes out that the mean size of Pt particles on the catalysts is about 15–17 nm which compares fairly well with that determined from TEM examination (Fig. 2a–d). Marginally, on a very different system (Pd/Montmorillonite), Veisz et al. showed a correlation between the fractions of high-coordination terrace sites (face atoms) and low-coordination defect sites (edge and corner atoms) and the crystallite size [26].

In Figs. 3–5, the kinetics of initial hydrogen adsorption at three different CO coverages are represented for Pt/C-ETEK, Pt/C-coll-C and Pt/C-coll-W, respectively. It must be noted that the lines through the data are a simple guide for the eye.

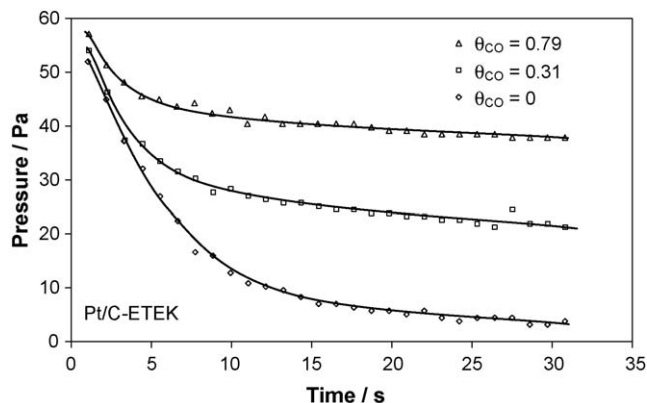


Fig. 3. Kinetics of hydrogen adsorption over Pt/C-ETEK at 353 K and different coverages of irreversibly bonded CO; (\diamond) $\theta_{\text{CO}} = 0$, (\square) $\theta_{\text{CO}} = 0.31$, (Δ) $\theta_{\text{CO}} = 0.79$.

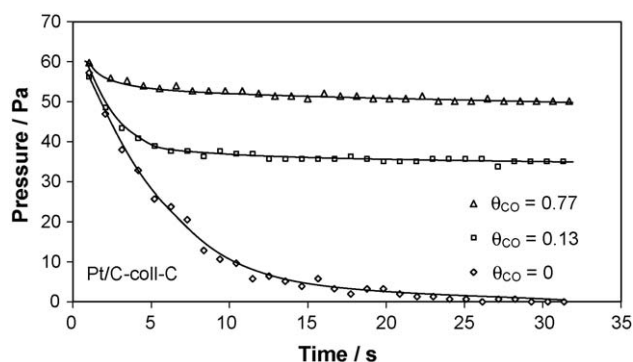


Fig. 4. Kinetics of hydrogen adsorption Pt/C-coll-C at 353 K and different coverages of irreversibly bonded CO; (\diamond) $\theta_{\text{CO}} = 0$, (\square) $\theta_{\text{CO}} = 0.77$, (Δ) $\theta_{\text{CO}} = 0.81$.

The initial rate of adsorption was calculated from the slope of the curves after 1 s, in the first 1–3 s, as mentioned above. Full hydrogen uptake is reached after 10–20 s. At longer times ($t > 15$ s), there is a slow decrease of hydrogen pressure which corresponds to the liberation of hydrogen covered platinum sites by spillover to the support [27]. This spillover rate appears to be one order of magnitude slower than the rate of hydrogen dissociation on platinum, under the present experimental conditions concerning temperature and pressure [28].

For the three catalysts, the initial rate of hydrogen adsorption has been calculated as a function of CO coverage (Table 2). From the initial rate, the TOF (turn over frequency, s^{-1}), i.e. number of hydrogen molecules dissociated per accessible Pt atom (N_s), was calculated. Hydrogen dissociation onto the Pt surface needs the occurrence of two neighboring CO-free Pt atoms to proceed: $\text{H}_2 + 2\text{Pt} \rightarrow 2\text{PtH}$. For a random distribution of adsorbed CO, the number of CO-free Pt atoms involved in pair sites will be, $N_s = \text{Pt}_s(1 - \theta_{\text{CO}})^2$. In contrast, for a distribution of CO adsorbed as islands, the number of CO-free Pt atoms involved in pair sites will be closer to: $N_s = \text{Pt}_s(1 - \theta_{\text{CO}})$. These two values of N_s were used to calculate TOF values according to CO distributions either at random or as islands.

At zero CO coverage, on CO-free Pt particles, the initial rates, and the associated TOF, of hydrogen dissociation are of the same order of magnitude whatever the catalyst (Table 2). A model for hydrogen dissociation has been proposed for metal particles exhibiting sites of various coordinations [29,30]. According to this model, hydrogen adsorption occurs via two pathways. The first one involves rapid dissociative adsorption at low-coordination sites to produce weakly bonded, highly mobile hydrogen atoms. The second pathway is the adsorption directly onto the basal planes (high-coordination) which occurs at an intrinsically lower rate.

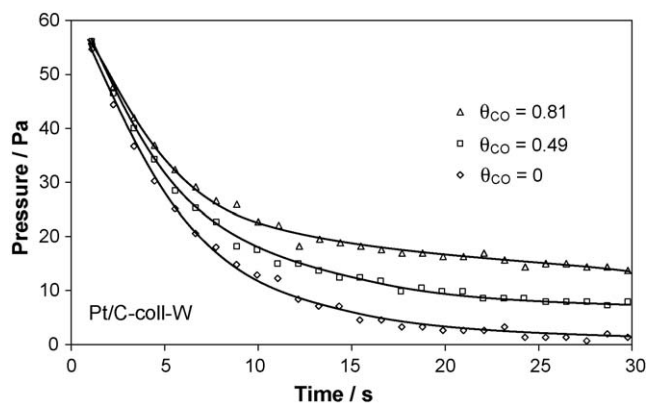


Fig. 5. Kinetics of hydrogen adsorption Pt/C-coll-W at 353 K and different coverages of irreversibly bonded CO; (\diamond) $\theta_{\text{CO}} = 0$, (\square) $\theta_{\text{CO}} = 0.49$, (Δ) $\theta_{\text{CO}} = 0.81$.

Table 2

Initial rate and turnover frequencies of hydrogen adsorption on the sample at various CO coverages (initial hydrogen pressure: 0.50–0.6 Pa, T : 353 K, sample mass: 0.140 g).

Sample	θ_{CO}	Initial rate (Pa s^{-1})	Turnover frequency ($\text{s}^{-1} \times 10^3$)	
			TOF ₁ , with $N_s = \text{Pt}_s$ ($1 - \theta_{\text{CO}}$)	TOF ₂ , with $N_s = \text{Pt}_s$ ($1 - \theta_{\text{CO}}$) ²
Pt/C-coll-C	0.00	3.59	5.87	5.87
	0.13	1.46	3.78	4.34
	0.39	0.53	4.40	7.22
	0.77	0.40	5.90	25.6
Pt/C-coll-W	0.00	3.86	7.40	7.40
	0.11	3.46	7.26	8.15
	0.22	3.46	8.00	10.2
	0.49	3.06	11.5	22.6
	0.81	2.53	27.8	146.0
Pt/C-EOTEK	0.00	3.19	8.42	8.42
	0.07	2.53	8.40	9.00
	0.31	1.60	8.52	12.3
	0.50	1.00	10.6	21.1
	0.79	0.68	14.0	66.5

Since the weakly bonded hydrogen adsorbed at low-coordination sites is highly mobile, those species can migrate to strongly bonded state very fast. This so-called portal model of hydrogen adsorption was demonstrated on model RuAg/silica catalysts [29,30], and extended to Pt/SiO₂ [11] silica because it was earlier shown on single crystals that hydrogen adsorption and dissociation is more efficient on low coordination Pt sites [31]. Analyzing our results in the frame of this model, we may postulate that the three catalysts exhibit a similar number of low-coordinated Pt atoms (defects, edges, corners) at the surface. This is rather in agreement with the close values of Pt dispersion, hence of surface Pt atoms (Table 1) and of mean size Pt particles from TEM examination (Figs. 2–3). However, this comment should be taken with care because Pt particles of the same size but exhibiting various crystal habits may expose different proportions of low or high coordination sites at the surface.

Another more important feature is the evolution of the initial rate of hydrogen adsorption as a function of CO coverage. The rate decreases by 5–10 times for Pt/C-EOTEK and Pt/C-coll-C, respectively, but it is only marginally affected for Pt/C-coll-W. This is reflected by a small increase of TOF₂ on Pt/C-coll-C, but a twentyfold increase on Pt/C-coll-W. To comment this behaviour, it is necessary to have some idea about the site distribution and site preference, of adsorbed CO as a function of coverage. Does it favor edges or planes? Is it random or in islands-like fashion? To our knowledge, there are very few studies dealing with this topic. On stepped Pt crystals, Leibsle et al. proposed a model describing the preference of CO to adsorb on all step sites first [32], in one-dimensional islands, and then to grow two-dimensional islands on terraces. In that case, the preference for CO to adsorb on steps was greater than the preference to adsorb on terraces, and the preference to adsorb as islands was greater than the preference to seek separated sites at random. Brandt et al. [33] extended this model to Pt/SiO₂ which includes concerning adsorption of CO on the Pt particles a preference to adsorb at corner or edges and a preference for island growth. To summarize, this model implies island growth beginning at low-coordination sites and spreading across the faces.

These considerations allow us to draw a picture of hydrogen dissociation, assuming that its intrinsic rate constant (per pair Pt site) is not affected by the presence of adsorbed CO. This is a reasonable hypothesis according to the theory of chemisorption developed by Hammer and Norskov [34]. This theory predicted an increase of binding energy and adsorption rate when the d-band center shifts up to the Fermi level.

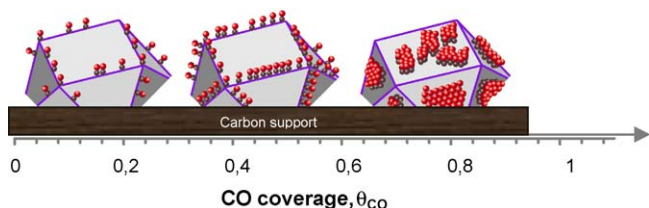


Fig. 6. Schematic interpretation of the CO adsorbed species distribution as a function of coverage. At low CO coverage, CO molecules could be chemisorbed onto low coordination surface sites whereas at high CO coverage, CO molecules could be preferentially chemisorbed onto the planes of cubooctahedra Pt aggregates.

Experimentally, Toolenaar et al. demonstrated by infrared studies of $^{12}\text{CO}/^{13}\text{CO}$ adsorption on Pt catalysts that little electronic modification (ligand effect) occurred upon increase of CO coverage [35]. Since there is little electronic modification of Pt d-band, little effect on hydrogen dissociation rate can therefore be expected.

The near constancy of TOF_1 up to $\theta \sim 0.5$, whereas TOF_2 tends to increase, could indicate that the site distribution of adsorbed CO indeed agrees with the model described above [33]: CO islands formation starting from edges and spreading across the faces with similar probability. On that account, TOF_1 appears more relevant to describe the intrinsic turnover frequency on a pair Pt site. At high CO coverage ($\theta \sim 0.8$) the Pt/C-coll-W catalyst attracts attention with a fourfold increase of TOF_1 , with respect to that on CO-free Pt surface, whereas for the two other catalysts TOF_1 remains constant or increases only slightly. We may put forward two proposals, at least, to explain the peculiar behavior of Pt/C-coll-W:

1. At high CO coverage of Pt/C-coll-W, there is a reconstruction of CO islands on the faces with some depopulation of CO adsorbed on low-coordination sites. It is generally recognized that CO-surface migration is low at room temperature, but will become easier above 353 K. A schematic interpretation is given in Fig. 6.
2. A CO-induced restructuring (surface flexibility) [36]. This reconstruction of the Pt surface may depend on the proportion of the various crystallographic planes, the interaction with the support or even the presence of impurities. This phenomenon is therefore depending on the history of the catalyst preparation, which is different for the three samples. More precisely, the activation procedures (and therefore temperature) could be at the origin of the differences between initial rates of hydrogen dissociation for the three catalysts. It is worth noting that at 353 K, hydrogen dissociation is one order of magnitude faster than hydrogen spillover from platinum particles to the carbon support [36].

It must be remembered that our aim in this paper was to determine the initial rate of dissociation of hydrogen as a function of CO poisoning. A few interpretations are given already in this paper but other interpretations may apply and the understanding of this very interesting, but rather complex behavior needs further in depth studies which are planned in the future.

4. Conclusion

To our knowledge, this is the first time that, in view of fuel cell applications, initial rates of hydrogen dissociation on

various Pt/C catalysts poisoned with CO have been determined. The constancy of TOF for hydrogen dissociation at zero CO coverage is globally in agreement with the current views for the kinetics of hydrogen dissociation and CO adsorption on metal particles. In particular, it is worth noting at high CO coverage (~ 0.8), that a Pt/C catalyst prepared using a colloidal process shows a low sensitivity to CO poisoning with an increase of TOF for hydrogen dissociation by one order of magnitude. This is an important matter for fuel cell application which demonstrates that according to the way by which the catalyst is prepared, Pt/carbon catalysts with the same support and comparable Pt particle sizes may exhibit very different sensitivities of hydrogen dissociation to CO poisoning.

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